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37

**A Chemical Study
of Rain and Stream Waters
in the Scottish Highlands**

By A. V. HOLDEN, B.A.

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of Rain and Stream Waters
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By A. V. HOLDEN, B.A.

Freshwater Fisheries Laboratory, Pitlochry

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A Chemical Study of Rain and Stream Waters in the Scottish Highlands

INTRODUCTION

For a number of years chemical analyses have been made by the Freshwater Fisheries Laboratory at Pitlochry of loch and stream waters in the Scottish Highlands, partly in conjunction with studies of biological productivity assessed mainly by measurement of bottom fauna populations. It was evident at an early stage in these investigations that the composition of the precipitation falling in the area had a marked influence on that of the stream waters, with respect to certain elements. As the geology of the Highlands is not generally conducive to the production of surface waters of high chemical content this atmospheric influence is often very significant, especially in coastal areas.

As no part of Scotland is more than about 110 km. from the sea, and the prevailing winds are from the Atlantic Ocean to the west, sea-spray exerts a dominant influence on the composition of precipitation, and consequently on that of much of the surface water of the Highlands. This paper describes a study made of two streams in the area, and of the precipitation giving rise to these streams, over a period of twelve months from March 1962 to March 1963.

SAMPLING SITES AND TECHNIQUE

Two unpolluted streams were chosen for the study in areas where other biological investigations were in progress. The first was Allt a'Chomair (in Strath Bran, Ross-shire) a small hill stream of low productivity, draining from siliceous granulites and mica-schists, with overlying peat. The second stream, the Shelligan Burn, is situated in Perthshire, about 160 km. to the SSE of the first site. It also drains from peat overlying quartzite, but in the lower part of its course is on Old Red Sandstone, drift-clay and gravel, which render it much more productive biologically than Allt a'Chomair.

A site was chosen on each stream for the collection of samples of precipitation. Such samples were also collected in the grounds of the laboratory at Faskally, about 23 km. to the north of the Shelligan site but no suitable stream was available here. Faskally is approximately 110 km., Shelligan about 100 km. and Allt a'Chomair about 45 km. from the Atlantic coast.

The samples of precipitation were collected in 20 cm. diameter polythene funnels fitted into 4-litre polythene bottles. The latter were shielded from solar radiation by polished aluminium sheeting to prevent excessive heating and evaporation, and were positioned to avoid water draining into the funnels from vegetation. The rim of each funnel was approximately 35 cm. from the ground. Around the periphery of each funnel there was a series of vertical rods, their lower ends fixed in a metal ring and the upper ends free. These rods prevented birds from perching on the funnel and fouling the samples. Glass wool plugs, renewed when necessary, were inserted in the funnel stems to prevent debris and insects from entering the bottles.

The bottles were emptied at approximately two-weekly intervals, or after a period necessary to collect sufficient water for analysis. At the Shelligan and Strath Bran sites the streams were sampled at the same time.

ANALYTICAL METHODS

The pH and bicarbonate alkalinity were measured electrometrically, using a Cambridge pH meter and glass electrode, and titrating to a pH of 5.0 with 0.02 N sulphuric acid for the alkalinity. Magnesium was determined spectrophotometrically with Titan yellow, the total hardness (calcium + magnesium) by titration with sodium versenate, and calcium by difference between the two determinations. Sodium and potassium were measured with an EEL flame photometer. Chloride was determined by potentiometric titration, using a silver-silver chloride electrode and a sodium acetate buffer as described by Shiner and Smith (1956). Free ammonia was estimated by Nessler's reagent, and nitrate by a modified phenoldisulphonic acid method which made allowance for any natural yellow colour in the samples, or derived from the reaction of any organic matter with the sulphuric acid present in the reagent.

All concentrations were calculated in terms of micro-equivalents per litre. As no method for sulphate of sufficient sensitivity and accuracy was available, sulphate concentrations were calculated as the difference between the sum of the cations (H^+ , Na^+ , K^+ , Mg^{++} , Ca^{++} and NH_4^+) and other anions (Cl^- , HCO_3^- and NO_3^-). The error inherent in the sulphate concentrations so estimated is obviously greater than that of the other determinations, but a few measurements made of high sulphate concentrations by a conductimetric method suggested that the calculation by difference was justified. This is also borne out by the findings of Gorham (1955) who used Mackereth's (1955) conductimetric method for the direct determination of sulphate. For comparison with the published data of other workers the concentrations in this report have been transformed to units of milligrams per litre (mg./l.).

COMPOSITION OF PRECIPITATION

Over the period of twelve months from mid-March 1962 to mid-March 1963 a total of 19 samples of precipitation were collected at each of the Shelligan and Strath Bran sites, and 21 at Faskally. The samples may be compared either in terms of the concentrations of the major ions found or of the masses of these ions deposited per unit area at each site. The concentrations in the samples were sometimes very low and in consequence the analytical errors relatively large so that the ratios between the concentrations of ions in individual samples could be grossly inaccurate. The total masses of the various ions have therefore been calculated over periods of six or twelve months, and the mean concentrations, or mass ratios, derived from them, so reducing the effects of random errors considerably.

(a) *Masses Deposited*

Examining firstly the masses (kg./ha.) of ions deposited at each site over the year (Table 1), the chloride, sodium and magnesium were highest at Strath Bran and lowest at Faskally, which is farthest from the sea. The chloride/sodium ratio (Table 2) was almost the same at all sites, and only slightly less than that of sea water. The magnesium/sodium ratios were similar at Strath Bran and Faskally, and again rather less than that in sea water. At Shelligan, by comparison with sea water, the amount of magnesium was about 60% high in proportion to the sodium found. By comparison with the sea water

TABLE 1

MASSES OF IONS (kg./ha.) DEPOSITED PER YEAR (12/3/62-14/3/63) AT THREE SITES

	S	Cl	NO_3-N	NH_4-N	Na	K	Mg	Ca	Precipitation (mm.)
Strath Bran	7.54	82.80	0.35	0.86	47.20	2.30	4.59	5.92	1352
Faskally	7.53	19.90	1.02	1.63	11.50	1.44	1.21	5.49	697
Shelligan	18.30	32.30	1.97	4.73	18.45	2.45	3.52	6.71	1040

TABLE 2

RATIOS TO SODIUM OF MASSES OF MAJOR IONS IN PRECIPITATION, 12/3/62-14/3/63

	S	Cl	K	Mg	Ca
Strath Bran	.16	1.76	.05	.10	.13
Faskally	.66	1.73	.13	.11	.48
Shelligan	.99	1.75	.13	.19	.36
Sea water	.084	1.80	.036	.121	.038

ratio the amount of potassium deposited at Strath Bran was about 40% higher, but at the two other sites the K/Na ratios were more than three times that of sea water. The masses of the other two major ions, calcium and sulphate, are interesting in that they are similar at the three sites, with the exception of the sulphate found at the most southerly site (Table 1). This latter anomaly may be due to the influence of atmospheric pollution from the central industrial belt of Scotland. That the major source of these two ions is not directly sea spray is made clear from the ratios to sodium at each site. The ratios differ widely between sites, and in all cases are much greater than the sea water values (Table 2). Finally, the masses of the two forms of nitrogen show a considerable increase from north to south, again suggesting the possible influence of atmospheric pollution.

Assuming that the sodium, chloride, magnesium and at least a part of the potassium in the deposits are derived from cyclic salts or airborne sea spray, it would seem probable that the prevalence of higher wind speeds during the winter might produce a closer similarity of the respective ionic ratios to those of sea water in winter than in summer. For the purpose of such a comparison, the precipitation at the three sites for the six months from mid-March to mid-September (summer period) and mid-September to mid-March (winter period) has been compared in Table 3.

As might be expected if wind influence is dominant, the masses of chloride, sodium, potassium and magnesium at each site were higher in winter than in summer, although in the case of potassium the differences were not large. The masses of calcium were, however, surprisingly similar at the three sites for the two periods, with the exception of the winter period at Faskally. The masses of sulphate were very similar in summer and winter at Strath Bran, but at the other sites the winter values were appreciably higher. Both forms of nitrogen were in greater quantity in winter at all sites, but again the two southern sites showed the more marked difference.

(b) *Ionic ratios*

An examination of the ratios of the masses of the other ions to those of sodium reveals differences between the two periods (Table 4). The Cl/Na ratio showed little variation at Strath Bran, although the winter value was rather closer to that of sea water. At the other two sites, however, it exceeded the sea water value slightly in winter, but showed a considerable deficiency of chloride in summer. In contrast, the summer values of the sulphate/sodium ratio were greater than the winter values at all three sites, suggesting that there had been some replacement of chloride by sulphate during the period. Eriksson (1960) discussed the possibility of sulphate from sulphuric acid releasing chloride from salt particles in the atmosphere. There is presumably a decrease in the extent of this process during the winter, as the chloride/sodium ratio is then much closer to that of sea water.

The magnesium/sodium ratio showed little seasonal variation at Strath Bran or Faskally, but at Shelligan the excess magnesium proved to be greater in summer than in winter. The potassium/sodium ratio also showed little difference between summer and winter at Strath Bran, but at the other two sites the summer ratios were the greater. The excess potassium at these latter sites, by comparison with sea water was about three times as large in summer as in winter. The calcium/sodium ratios were also greater in summer at all sites, and particularly at the two southern sites.

Thus if the mass of a particular constituent was appreciably in excess of that expected from the sea water ratio, as in the case of calcium, potassium and sulphate, the excess was greater in summer than in winter. For chloride and magnesium, which were approximately in the ratio expected for sea water, the summer-winter changes were comparatively small.

Although there were considerable differences between individual samples of precipitation at any one site, both as regards the concentrations of ions found and the ratios relative to sodium, there was nevertheless a consistency between the sites. On most occasions the mass of each ion deposited at Faskally was less than that deposited at Shelligan, Faskally being somewhat more sheltered, but subject to the same meteorological influences. The masses of the ions deposited at the most northerly site varied independently of those at the other sites, due probably to the different local meteorological conditions influencing that area.

The evidence for a greater proportion of cyclic salts being present in winter precipitation is provided not only by the larger masses of the major ions of sea water deposited, namely chloride, sodium and

TABLE 3
MASSES OF IONS (kg./ha.) DEPOSITED DURING SUMMER AND WINTER PERIODS

	S	Cl	NO ₃ -N	NH ₄ -N	Na	K	Mg	Ca	Precipitation (mm.)
Summer 12/3/62-13/9/62									
Strath Bran	3.84	32.80	0.12	0.33	19.00	0.99	2.01	3.04	772
Faskally	2.88	5.15	0.40	0.43	3.62	0.71	0.39	3.29	354
Shelligan	6.10	6.25	0.62	0.88	4.60	1.09	1.08	3.31	515
Winter 14/9/62-14/3/63									
Strath Bran	3.70	50.00	0.23	0.53	28.20	1.31	2.58	2.88	580
Faskally	4.65	14.75	0.62	1.20	7.88	0.73	0.28	2.20	343
Shelligan	12.20	26.05	1.35	3.85	13.85	1.36	2.44	3.40	525

TABLE 5
MEAN ANALYSES OF STREAMS DURING SUMMER AND WINTER PERIODS
(CONCENTRATIONS IN mg./l.)

	Concn	S	Cl	CO ₃ ^a	NO ₃ -N	NH ₄ -N	Na	K	Mg	Ca
Strath Bran										
Summer	Ratio to Na	1.57 0.23	12.14 1.74	3.45 —	0.09 —	0.28 —	6.97 —	0.39 0.056	1.03 0.15	1.94 0.28
Winter	Ratio to Na	1.38 0.28	8.02 1.63	3.50 —	0.12 —	0.30 —	4.93 —	0.39 0.079	0.79 0.16	1.58 0.32
Shelligan										
Summer	Ratio to Na	2.51 0.69	5.15 1.41	20.5 —	0.05 —	0.08 —	3.64 —	0.25 0.069	1.91 0.52	7.76 2.13
Winter	Ratio to Na	2.00 0.60	4.83 1.45	18.9 —	0.11 —	0.08 —	3.34 —	0.26 0.078	1.57 0.47	7.22 2.16

^a Alkalinity as CaCO₃

TABLE 4

RATIOS TO SODIUM OF MASSES OF MAJOR IONS IN PRECIPITATION DURING SUMMER AND WINTER PERIODS

		S	Cl	K	Mg	Ca
Summer 12/3/62-13/9/62	Strath Bran	·20	1·73	·05	·11	·16
	Faskally	·80	1·42	·20	·11	·91
	Shelligan	1·33	1·36	·24	·24	·72
Winter 14/9/62-14/3/63	Strath Bran	·13	1·77	·05	·09	·10
	Faskally	·59	1·87	·09	·10	·28
	Shelligan	·88	1·88	·10	·18	·25
	Sea water	·084	1·80	·036	·121	·038

magnesium, but also by the closer approach to the sea water ratios of the values for potassium and calcium. The position of sulphate is more complicated, as an appreciable proportion of this ion at the two more southerly sites is probably derived from atmospheric pollution originating in the central industrial belt of Scotland to the south.

COMPOSITION OF STREAM WATERS

The two streams investigated were sampled whenever the precipitation samples were collected. Although it was originally intended that this would enable the stream composition to be compared with that of the precipitation which had fallen during the preceding sampling interval, the variation in the streams was very much less than that in the precipitation. The comparison can only be made between the concentrations of ions, and not the masses, as the stream flow-rates were not measured.

The mean values of the concentrations of each ion were calculated over the summer and winter periods, and are compared in Table 5, together with the ratios with respect to sodium. There is a greater difference between the two periods at Strath Bran in the concentrations of chloride and sodium than occurred at Shelligan, but otherwise the levels are reasonably constant. This is particularly true for the bicarbonate alkalinity, although under flood conditions this component is known to decrease markedly. The streams were sampled in various states of flow, although flood conditions were usually avoided, but the agreement between the summer and winter mean values is surprising.

The range of alkalinity values obtained in the samples for the year at Strath Bran was 0·8-9·4 mg./l (as CaCO_3), and at Shelligan 12·0-33·6 mg./l (as CaCO_3) (excluding one value of 1·8 mg./l at the latter site following a sudden snow-melt). The concentrations of nitrate were higher in winter than in summer, but the mean ammonia concentrations were similar.

The ratios of the other major ions to sodium do not show any marked seasonal variation, in contrast to the ratios for precipitation. The general impression gained from the results is of considerable stability in the composition of the stream waters, which show little influence of the considerable fluctuations occurring in the precipitation of the catchment areas. The relations between the two series of samples are discussed fully in the next section.

COMPARISON OF PRECIPITATION AND STREAM ANALYSES

To make this comparison, it is necessary to convert the precipitation data, hitherto expressed in units of mass per unit area, to concentration units by dividing by the total rainfall over the periods concerned. The mean ionic concentrations can then be compared directly with the mean stream concentrations over the same sampling periods (Table 6).

(a) Concentrations

The concentrations in summer of sodium and chloride in the streams were three to four times those found in the precipitation, while in the winter they were almost equal. Loss of water by evaporation or transpiration in summer is too small to account for the large difference between summer and winter

TABLE 6
COMPARISONS OF PRECIPITATION AND STREAM ANALYSES
(CONCENTRATIONS IN mg./l.)

Strath Bran	Summer	Stream Rain Ratio	S	Cl	NO ₃ -N	NH ₄ -N	Na	K	Mg	Ca
			1.57	12.14	0.091	0.28	6.97	0.39	1.03	1.94
			0.50	4.22	0.016	0.04	2.46	0.12	0.26	0.4
			3.1	2.9	6	7	2.8	3.3	4.0	4.9
	Winter	Stream Rain Ratio	1.38	8.02	0.13	0.30	4.93	0.39	0.79	1.58
			0.64	8.62	0.04	0.09	4.88	0.23	0.45	0.50
			2.2	0.9	3	3	1.0	1.7	1.8	3.2
	Summer	Stream Rain Ratio	2.51	5.15	0.05	0.08	3.64	0.25	1.91	7.76
			1.18	1.21	0.12	0.17	0.90	0.20	0.21	0.64
			2.1	4.3	0.4	0.5	4.0	1.2	9.1	12.1
	Winter	Stream Rain Ratio	2.00	4.83	0.11	0.08	3.34	0.26	1.57	7.22
			2.32	4.93	0.26	0.73	2.55	0.26	0.46	0.64
			0.9	1.0	0.4	0.1	1.3	1.0	3.4	11.2

concentrations. The implication is that in summer most of the sodium and chloride is deposited in the dry state, probably by salt capture on vegetation, and is subsequently washed into the streams. In winter this means of deposition becomes insignificant, all the chloride and sodium entering the streams from precipitation. The slight excess of sodium in the Shelligan Burn in winter, compared with that in the winter rain, may possibly be due to some influence of the summer deposition extending into the so-called winter period, or more likely to a contribution from geological sources, as is discussed later with reference to calcium and magnesium.

The potassium concentrations in the Shelligan rain and stream were similar in summer and winter, but at Strath Bran the mean stream concentrations were significantly greater than those in the precipitation, although less so in winter than in summer. The concentrations found were, however, too low to be regarded as more than approximate.

The stream/rain ratios for magnesium were greater in summer than in winter at both sites, following the examples of sodium and chloride, as would be expected if the magnesium were derived partly from cyclic salts. However, at Shelligan particularly, the stream concentrations were greatly in excess of those in the precipitation even in the winter, indicating the probable derivation of most of the magnesium at this site from ground sources. The same is true of calcium, for which at Shelligan the stream concentrations are so much greater than those in the rain both in summer and winter that the contribution from cyclic salts must be very small. At Strath Bran a significant amount of calcium is derived from cyclic salts, and the stream/rain ratio shows an appreciable decrease from summer to winter. The stream/rain ratio for sulphate also shows a decrease from summer to winter at both sites, and at Shelligan the mean concentrations in the stream and rain samples were almost the same during the winter.

The two forms of nitrogen are interesting in that, whereas at Strath Bran the stream concentrations were consistently higher than in the rain, at Shelligan they were consistently lower. In the winter particularly, the concentrations in some of the precipitation samples at Shelligan were unusually high, especially during falls of snow. The mean ammonia-nitrogen concentrations in the stream at Strath Bran were more than twice those of nitrate-nitrogen, while at Shelligan the mean concentrations were approximately the same. It is possible that the higher proportion of oxidised nitrogen present in the Shelligan is related to the higher pH and calcium concentration, and the associated bacterial activity.

(b) *Ionic ratios*

Examining the mean ratios to sodium of all the other ions in both streams and precipitation at the two sites (Table 7), the proportion of chloride approximates fairly closely to that of sea water during both summer and winter at Strath Bran. At Shelligan, while during the winter the rain also resembles sea water in this respect, in the summer there is a deficiency of chloride (or alternatively an excess of sodium). At this site the stream samples in both periods showed the same marked deficiency.

At Strath Bran the stream ratios in summer closely resembled those of the precipitation except for significant excesses of magnesium and calcium, assumed to be derived from geological sources. There is also little change in the stream from summer to winter, but the values for rain show some decrease in

TABLE 7

COMPARISON OF RATIOS TO SODIUM IN PRECIPITATION AND STREAM ANALYSES							
			S	Cl	K	Mg	Ca
Strath Bran	Summer	Rain	·20	1·73	·05	·11	·16
		Stream	·23	1·74	·06	·15	·28
	Winter	Rain	·13	1·77	·05	·09	·10
		Stream	·28	1·63	·08	·16	·32
Shelligan	Summer	Rain	1·33	1·36	·24	·24	·72
		Stream	·69	1·41	·07	·52	2·13
	Winter	Rain	·88	1·88	·10	·18	·25
		Stream	·60	1·45	·08	·47	2·16
Sea water		·084	1·80	·036	·121	·038	

sulphate and calcium. At Shelligan also there is little change in stream ratios between the periods, with the winter rain again relatively deficient in sulphate and calcium, and in this case also in magnesium. The very high potassium/sodium ratio in the summer rain at Shelligan, already referred to, was paralleled by a similar excess at Faskally. Finally, comparison of stream and rain ratios indicates the much greater proportion of non-atmospheric magnesium and calcium at Shelligan.

(c) *Sources of ions*

To assess the proportion of the major ions contributed by terrestrial sources it is necessary to compare the ratios of the other ions to chloride, rather than to sodium, as has been done for precipitation. Some sodium in surface waters may be derived from geological formations, and perhaps also from atmospheric pollution in some areas, but it is generally accepted that the fraction of chloride from ground sources, at least in igneous rock areas, averages not more than 5% (Conway, 1942) and less in maritime regions. Eriksson (1955) estimated the chloride derived from bedrock in Scandinavian rivers to be not more than 1-2%. The ratios to chloride for the mean summer and winter concentrations in rain and stream samples are compared in Table 8.

TABLE 8

COMPARISON OF RATIOS TO CHLORIDE IN PRECIPITATION AND STREAM ANALYSES

			S	Na	K	Mg	Ca
Strath Bran	Summer	Rain	·12	·58	·03	·06	·10
		Stream	·13	·57	·03	·09	·16
	Winter	Rain	·07	·57	·03	·05	·06
		Stream	·17	·61	·05	·10	·20
Shelligan	Summer	Rain	·98	·74	·17	·17	·53
		Stream	·49	·71	·05	·37	1·51
	Winter	Rain	·47	·52	·05	·09	·13
		Stream	·41	·69	·05	·32	1·49
		Sea water	·047	·555	·020	·067	·021

At Strath Bran there is little evidence of sodium from terrestrial sources at any time, and in summer this is also true of both sulphate and potassium. In winter about half the sulphate and potassium in the stream were from ground sources, possibly as the result of the decomposition of vegetation. About one-third of the magnesium and calcium were of terrestrial origin in summer, with half the magnesium and two-thirds of the calcium so derived in winter.

At Shelligan there was no evidence in summer of any sodium of terrestrial origin, but in winter this component constituted about one-quarter of the total. The sulphate falling in precipitation appears to be largely removed from solution in summer, but this effect was of less significance in winter, while the same was true of potassium. On the other hand, most of the magnesium and calcium in the stream was from ground sources at all times, in winter as much as 90% of the calcium and 70% of the magnesium. The source of these ions is probably the Old Red Sandstone formation in the lower reaches of the stream, just above the sampling site.

COMPARISON WITH OTHER SCOTTISH PRECIPITATION DATA

It has been shown so far that the composition of stream waters may be very dependent on that of the precipitation in the respective catchment areas. The composition of the precipitation is partly dependent on geographical location, and perhaps in part to atmospheric pollution. The influence of both factors is likely to vary from year to year. Although the major proportion of the dissolved salts is derived from sea water, the calcium and sulphate appear to be largely independent of this source. Further information on this aspect can be obtained by a comparison of the data from the three inland sites with that from the five Scottish synoptic stations which have for some years formed part of a European network for precipitation and air sampling. The samples at these stations are taken each calendar month, and for comparison with the three inland sites the data for the period April 1962-March 1963 have been used. The masses of the major ions deposited, and the ratios to sodium, are given in Tables 9 and 10.

The amounts of sodium and chloride deposited vary widely, the exposed island stations at Stornoway and Lerwick having the highest quantities. An examination of the ratios of other ions to sodium (Table 10) shows that the values for Edinburgh are anomalous, the chloride/sodium ratio in particular being very low. This relationship existed in almost all rain samples during the period, although ratios before mid-1959 had been normal. Apart from Edinburgh, the stations showed a close similarity to sea water in the Cl/Na and Mg/Na ratios. The K/Na ratios at Stornoway and Lerwick were similar to that at Strath Bran (0.05), while those of Aberdeen and Eskdalemuir were nearer to the values calculated for Faskally and Shelligan. The S/Na and Ca/Na ratios at Stornoway and Lerwick were largely influenced by the high deposition of marine salts, while at Aberdeen and Eskdalemuir there were appreciable quantities of non-marine sulphate and calcium.

If the proportion of any ion derived from marine salts (calculated from the chloride deposited) is deducted from the total deposit of that ion, the residue is termed the 'excess'. The values of these excess deposits for the five Scottish synoptic stations and the three inland sites are given in Table 11 for the period April 1962-March 1963. Apart from the value for Edinburgh, which seems likely to have been affected by pollution, there is a fairly uniform deposition of non-marine calcium in precipitation of 4-6 kg./ha. For an annual rainfall of 800 mm., this is equivalent to a concentration of 0.5-0.75 mg./l., a higher rainfall giving a proportionately lower concentration. This level is to be expected in surface waters in the absence of dissolved lithospheric calcium or marine salts. Surface waters with a chloride concentration of the order of 5 mg./l. assumed to be entirely of marine origin, would also contain 0.1 mg./l of calcium associated with the chloride. Thus even where the chloride level is as high as 20 mg./l. any calcium in excess of about 1.0 mg./l. must be derived from terrestrial, usually lithospheric, sources.

The values for excess sulphate show less uniformity, but while the non-marine calcium probably exists as the sulphate, further sulphate may be derived from atmospheric pollution, or oxidation of gaseous hydrogen sulphide emanating from the decomposition of vegetation or mud deposits as discussed by Eriksson (1960). Calculation of the mean annual pH values of the precipitation at the three inland sites by the method of Barrett and Brodin (1955), in which the average hydrogen concentration is

TABLE 10

RATIOS TO SODIUM OF MASSES OF MAJOR IONS IN
PRECIPITATION (APRIL 1962-MARCH 1963)

	S	Cl	K	Mg	Ca
Stornoway	·10	1·77	·063	·13	·060
Lerwick ^a	·14	1·72	·047	·17	·066
Aberdeen	·37	1·56	·090	·13	·196
Edinburgh	·18	0·49	·048	·02	·382
Eskdalemuir ^b	·58	1·77	·104	·18 ^c	·156
Sea water	·084	1·80	·036	·121	·038

a No sample for March 1963

b Figures for June 1962 not available

c 0·13, excluding March 1963

TABLE 9

MASSES OF IONS (kg./ha.) DEPOSITED PER YEAR (APRIL 1962-MARCH 1963) AT SYNOPTIC STATIONS									
	S	Cl	NO ₃ -N	NH ₄ -N	Na	K	Mg	Ca	Precipitation (mm.)
Stornoway	28.77	501.94	8.62	10.30	283.25	17.92	35.47	16.93	788
Lerwick ^a	19.41	234.80	1.30	0.67	136.26	6.38	23.78	8.95	585
Aberdeen	14.76	62.50	2.76	2.84	40.02	3.60	5.19	7.84	796
Edinburgh	10.79	28.74	5.08	0.70	58.77	2.84	1.35	22.43	731
Eskdalemuir ^b	13.19	40.01	1.01	1.71	22.58	2.35	4.05	3.52	1269

^a No sample for March 1963

^b Figures for June 1962 not available

TABLE 12

MEAN ANNUAL RATIOS TO SODIUM IN PRECIPITATION AT STORNOWAY AND LERWICK (1958-1963)									
	S	Cl	K	Mg	Ca	Na deposited (kg./ha.)	Precipitation (mm.)		
Stornoway	1958	.16	.042	.12	.065	82.51	580		
	1959	.10	.043	.12	.053	628.68	1244		
	1960	.12	.042	.12	.038	558.40	1260		
	1961	.12	.066	.12	.045	181.71	816		
	1962	.10	.063	.13	.060	283.25	788		
	Mean	.12	.051	.12	.052				
Lerwick	1958	.13	.041	.14	.052	133.22	529		
	1959	.10	.037	.12	.047	915.36	954		
	1960 ^a	.11	.045	.11	.096	331.75	668		
	1961 ^b	.11	.043	.13	.081	278.81	851		
	1962 ^a	.14	.047	.17	.066	136.26	585		
	Mean	.12	.043	.13	.068				

^a 11 months

^b 10 months

estimated and reconverted to the pH notation, gives values of 4.40, 4.74 and 5.08 for Shelligan, Faskally and Strath Bran respectively. This increase in acidity in a southerly direction, paralleling the increase in excess sulphate, suggests that the source is sulphuric acid from atmospheric pollution, which is most probable near the central industrial region of Scotland.

TABLE 11
DEPOSITS OF EXCESS IONS (kg./ha.) AT SCOTTISH STATIONS
(APRIL 1962-MARCH 1963)

	S	Na	K	Mg	Ca
Stornoway	5.43	4.67	7.88	1.84	6.40
Lerwick ^a	8.48	5.95	1.68	8.05	4.02
Aberdeen	11.85	5.32	2.35	1.00	6.53
Edinburgh	9.45	42.82	2.26	-0.57	21.83
Eskdalemuir ^a	11.33	0.38	1.55	1.37	2.68
Strath Bran	3.69	1.25	0.64	-0.96	4.18
Faskally	6.60	0.46	1.04	-0.12	5.07
Shelligan	16.80	0.52	1.80	1.36	6.03

a 11 months only

Of the excesses of other ions in Table 11, those of Mg are small and fairly uniform, with the sole exception of Lerwick, the high value for which is due to an excessively high deposit in January 1963. The similarity of the values is in marked contrast to the wide range of the total magnesium deposits. The sodium excess is more variable and again the value for Edinburgh is suspect, but the Na/Cl ratio at this site is regularly much in excess of those at all other sites. The potassium values are also fairly uniform, with the exception of that for Stornoway. The size of the latter value is almost entirely due to an unusually high potassium deposit in March and August 1962, when the K/Na ratios were 0.42 and 0.59 respectively. The general impression from Table 10 is, however, that the non-marine deposits are fairly uniform over the country, in contrast to those of the marine salts.

One further variation in salt deposition must be considered before deductions can be made regarding the origins of the various ions in surface waters in Scotland. This is the annual fluctuation to be expected at any individual sampling site. The most complete data available in Scotland are from Stornoway and Lerwick, and in Table 12 the ionic ratios to sodium, together with other relevant information, are given for the period April 1958-March 1963. In each case the annual period refers to that beginning in April of the year stated.

With few exceptions, there is a considerable uniformity in the values for each ratio over the five years at the two stations. Most of the irregular yearly values are due to an exceptionally high or low deposition of the particular ion in an individual month, or over a short period of the year. The largest variation from year to year occurs in the Ca/Na ratio, but it will be seen by comparison with the ratios in Tables 2 and 9 that this is small relative to the values at other sampling sites. Over the five-year period, the rainfall and particularly the mass of sodium deposited varied considerably, and independently of each other, but the ionic ratios show a considerable degree of agreement with those of sea water.

DISCUSSION

The considerable influence of cyclic salts on the composition of coastal rain has been demonstrated by studies in many areas of the world, and notably by Sugawara *et al.* (1949) in Japan, Eriksson (1952) in Sweden, Gorham (1957) in Ireland and (1958) in England, Junge and Werby (1958) in the United States and Miller (1961) in New Zealand. Holden (1961) discussed the decrease in chloride content of surface waters with distance from the sea in various parts of the world.

The relatively small size of Scotland, and its position off the main European land-mass at the eastern boundary of the Atlantic Ocean, is responsible for the closer approximation to sea water of the ionic ratios of Scottish precipitation than has been recorded for most other countries. Thus the Cl/Na ratios in Scotland are generally between 1.7 and 1.8, whereas in Sweden Emanuelsson *et al.* (1954) found the range extended from over 1.2 near the south-west coast to less than 0.5 near the Baltic coast. Miller (1961) gives average values in New Zealand for periods of several months ranging from 1.3 to 2.2. Sugawara *et al.* (1949) in Japan found that the ratio increased from 1.8 at the coast to 2.4 inland. In the United States, Junge and Werby found the ratios to be in the range 0.5 to 1.0 well inland.

Of the other ratios, there is a general agreement that, for a maritime climate, the Mg/Na and K/Na ratios in rain are fairly close to those of sea water, while the Ca/Na and S/Na ratios are well in excess of sea water. The amounts by which these ratios exceed their counterparts in sea water are nevertheless generally smaller in Scottish precipitation than for continental rain. This preponderance of marine salts is emphasized by the higher rate of salt deposition in Scotland than over continental land masses. Yet the actual excesses of ions (over those due to marine salts) calculated in units of kg/ha from the chloride deposited are similar to those given by Eriksson (1960) for western Europe in 1958. The effects of these excesses on the ionic ratios for Scottish rain are reduced by the dominance of marine salt deposits.

Using the annual chloride deposition for comparison, Scottish values vary from about 20 kg./ha. inland to over 60 kg./ha. on the coast. Emanuelsson *et al.* (1954) gives values in the range 2.4–43.7 kg./ha. for Sweden, but most of the country receives less than 10 kg./ha. Miller (1961) recorded 116 kg./ha. on the coast of New Zealand. Eriksson (1960), surveying world data on chloride deposition, gives the range 0.1–36 kg./ha. for the United States, but most of that country receives less than 3 kg./ha. Values in Europe away from the coast are less than 20 kg./ha., and as low as 0.1 kg./ha. in Central Europe and northern Sweden. Only at exposed stations in the south-western extremities of Ireland, England and Norway were deposits in excess of 100 kg./ha., and thus comparable with those at Stornoway and Lerwick. The relation between the chloride content of surface waters and the distance from the sea was discussed by Holden (1961), who showed that for several sets of data from different localities the concentration C varied inversely with the distance D according to the empirical formula $C = KD^{-n}$, where K and n are constants. The value of n was approximately 0.33, while those for K varied from 0.32 to 1.49 depending on the locality.

Despite the high marine salt content of Scottish precipitation, there are significant excesses of potassium, and particularly of sulphate and calcium, in unpolluted areas. Using sodium as a reference, excesses of magnesium are very small or non-existent, while chloride is occasionally deficient. Junge and Werby (1958) believe that it is more likely that sodium is in slight or moderate excess, at least in the United States. This may be true for areas where cyclic marine salts are of lesser importance, as over continental land masses, especially if atmospheric pollution is significant. The excesses of sodium, potassium and calcium are regarded by Junge and Werby as due to cyclic mineral dust, while the excess sulphate is believed to be more uniform over the earth's surface and due to oxidation of hydrogen sulphide emanating from organic decomposition. They estimate the average excess of sulphate in precipitation to be 2.2 mg./l. (as sulphur). The average concentration of the excess sulphate in Stornoway and Lerwick precipitation over the period April 1959–March 1962, by comparison, were 3.0 and 3.3 mg./l. respectively.

Emanuelsson *et al.* (1954) published maps showing the values of the ionic ratios to sodium in Scandinavian precipitation. The ratio Ca/Na increased in a north-easterly direction from less than 0.3 north of Denmark to over 2.0 near the Baltic coast of Sweden. Comparison with Table 10 shows the much

smaller deviation of Scottish values from that of sea water. Similarly the ratio K/Na increased from less than 0.1 north of Denmark to a value in excess of 0.6 in central southern Sweden, again very much above the Scottish values. Only the data quoted by Gorham (1957) for Galway in Ireland show values as close to sea water as those of Scotland; Galway is exposed to the same oceanic influences from the west.

Less information has been published on the nitrogen content of precipitation but Angstrom and Hogberg (1952) found the annual deposition of ammonia-nitrogen in unpolluted Swedish rain varied from 1.03 kg./ha. in central Sweden to 3.73 kg./ha. in the south. Nitrate-nitrogen was on average almost exactly half that in the ammonia form. By comparison, deposits of ammonia-N in rain in Scotland varied from 0.67 kg./ha. at Lerwick to 10.30 kg./ha. at Stornoway, although the latter value seems unduly high. Apart from the Shelligan site, where atmospheric pollution may indeed be significant, the next highest value recorded was 2.84 kg./ha. at Aberdeen. There is no evidence from the Scottish data of a simple relationship between the nitrate and ammonia forms of nitrogen.

Eriksson (1955) concluded that much of the chloride in river waters must be precipitated from the atmosphere in some manner other than by rain and snow, and suggested that vegetation trapped condensation nuclei to the extent of several kg./ha. per year. He showed later (Eriksson, 1960) that the ratio of chloride in precipitation to that in rivers in Scandinavia averaged about 0.3. This value is close to that obtained during the summer for the Shelligan and Strath Bran streams, but the winter values for these areas were approximately unity. The reason for this difference is not clear, although it seems likely that the higher temperatures and relatively drier weather of the summer period would be more conducive to 'dry fallout'.

The precipitation of Scotland is dominated by the high proportion of marine salt, but the origins of the appreciable excesses of certain ions, principally calcium and sulphate but occasionally potassium, remain obscure. Magnesium in Scotland is generally only in small excess except in polluted areas, in contrast to the precipitation of Japan (Sugawara *et al.* 1949), where the Mg/Cl ratio increased five-fold with distance over 180 km. from the Pacific coast. The increases in the Ca/Cl and SO₄/Cl ratios over the same distance in Japan were also proportionately much greater than those found in Scotland. One possible source of excess potassium, other than atmospheric pollution, is in the pollen of vegetation, and particularly of trees. It may be significant that the two southern sites sampled in the present work are situated in well-wooded areas. Terrestrial sources of excess calcium are few in Scotland, and the observational sites at Stornoway and Strath Bran in particular are at a great distance from any limestone or other calciferous deposit. The excess sulphate, as suggested by Conway (1942), Eriksson (1960) and others, is most likely to be produced by the oxidation of hydrogen sulphide derived from the decomposition of organic matter, and particularly that in peat bogs, which cover a large proportion of Scotland.

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SUMMARY

1. A study has been made of the composition of precipitation at three inland sites in the Scottish Highlands over a period of twelve months, and the analyses compared with those of stream waters at two of the sites.
2. Analyses were made for pH, sodium, potassium, calcium, magnesium, chloride and bicarbonate, and nitrogen in both nitrate and ammonia forms.
3. The proportions of sodium, magnesium and chloride in precipitation were generally very similar to those of sea water.
4. The proportion of potassium was appreciably higher than in sea water, and those of calcium and sulphate greatly in excess of the sea water values.
5. The masses of calcium and sulphate deposited per annum at the three sites were similar, except for a greater deposition of sulphate at the most southerly site, believed due to atmospheric pollution. The masses of nitrogen in both nitrate and ammonia forms deposited during the year also increased from north to south, possibly due to atmospheric pollution.
6. Comparison of the masses of the various ions deposited in precipitation revealed differences between the periods mid-March to mid-September (summer) and mid-September to mid-March (winter). The masses of cyclic salts (predominantly sodium, magnesium and chloride) were greater during the winter period, but the masses of calcium and sulphate showed less variation. More nitrogen was deposited during the winter period, although the precipitation in the two periods was similar.
7. Stream analyses showed considerable uniformity during the year. There was evidence that during the summer period most of the cyclic salts were deposited in the dry state, and the concentrations of sodium and chloride in the streams were three to four times the mean values for summer precipitation. In winter the concentrations of these ions in streams and rain at each site were similar.
8. Estimates have been made of the proportions of sodium, potassium, magnesium, calcium and sulphate in the two streams contributed by terrestrial sources. These proportions were in most instances greater in winter than in summer.
9. The composition of precipitation at the three inland sites has been compared with that at the five Scottish synoptic stations (four coastal) over the same period.
10. The total salt deposits at the eight sites have been calculated for components of both marine and non-marine origin. The former (cyclic salts) decrease with distance from the coast, while the non-marine forms (excess salts) were fairly uniformly deposited.
11. The total salt deposited annually in Scotland is relatively high compared with continental areas, and is characterised by the high proportion of cyclic salt, even in inland areas.
12. The composition of the salts deposited at individual sites appears to be fairly constant from year to year, with a much greater variation between sites.

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